2008 LLNL Nuclear Forensics Summer Program

Lawrence Livermore National Laboratory
Chemistry, Materials, Earth and Life Sciences
Glenn T. Seaborg Institute
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Sponsors:
National Technical Nuclear Forensics Center, Domestic Nuclear Detection Office, Department of Homeland Security
LLNL: Glenn T. Seaborg Institute, Chemistry, Materials, Earth and Life Sciences Directorate

Glenn T. Seaborg Institute

LLNL-AR-407169

The Lawrence Livermore National Laboratory (LLNL) Nuclear Forensics Summer Program is designed to give both undergraduate and graduate students an opportunity to come to LLNL for 8-10 weeks during the summer for a hands-on research experience. Students conduct research under the supervision of a staff scientist, attend a weekly lecture series, interact with other students, and present their work in poster format at the end of the program. Students also have the opportunity to participate in LLNL facility tours (e.g. National Ignition Facility, Center of Accelerator Mass-spectrometry) to gain a better understanding of the multi-disciplinary science that is on-going at LLNL.

Currently called the Nuclear Forensics Summer Program, this program began ten years ago as the Actinide Sciences Summer Program. The program is run within the Glenn T. Seaborg Institute in the Chemistry, Materials, Earth and Life Sciences Directorate at LLNL. The goal of Nuclear Forensics Summer Program is to facilitate the training of the next generation of nuclear scientists and engineers to solve critical national security problems in the field of nuclear forensics. We select students who are majoring in physics, chemistry, nuclear engineering, chemical engineering and environmental sciences. Students engage in research projects in the disciplines of actinide and radiochemistry, isotopic analysis, radiation detection, and nuclear engineering in order to strengthen the 'pipeline' for future scientific disciplines critical to DHS, NNSA.

This is a competitive program with over 170 applicants for the 10 slots available. Students come highly recommended from universities all over the country. For example, this year we hosted students from UC Davis, Texas A&M, Univ. of Wisconsin, Univ. of Missouri, Georgia Tech, Iowa State Univ., Univ. of Nevada, Las Vegas, Univ. of South Carolina, and Arizona State Univ. We advertise with mailers and email to physics, engineering, geochemistry and chemistry departments throughout the U.S. We also host students for a day at LLNL who are participating in the D.O.E. sponsored "*Summer School in Nuclear Chemistry"* course held at San Jose State University and have recruited from this program.

This year students conducted research on such diverse topics as: isotopic fingerprinting, statistical modeling in nuclear forensics, nanomechanics, environmental radiochemistry, development of reactor fuel taggants, semiconductor detectors, actinide separations chemistry, development of automated chemistry methods, and anti-neutrino monitoring of nuclear reactors.

Graduate students are invited to return for a second year at their mentor's discretion. For the top graduate students in our program, we encourage the continuation of research collaboration between graduate student, faculty advisor and laboratory scientists. This creates a successful pipeline of top quality students from universities across the U.S. Since 2002, 20 summer students have continued to conduct their graduate research at LLNL, 4 have become postdoctoral fellows, and 7 have been hired as career scientists.

Seminar Schedule 2008

Date	Speaker	Title of Presentation
June 26	Ken Moody, LLNL	Forensic Radiochemistry
July 3	George Anzelon, LLNL	IAEA Investigations of Undeclared Nuclear Activities
July 10	Bill Dunlop, LLNL	Nuclear Weapons 101
July 17	John Perkins, LLNL	Fusion Energy
July 24	Jean Moran, LLNL	Forensic Hydrology
July 31	Jay Davis, former director of DTRA	A Functional Look at the Nuclear Force

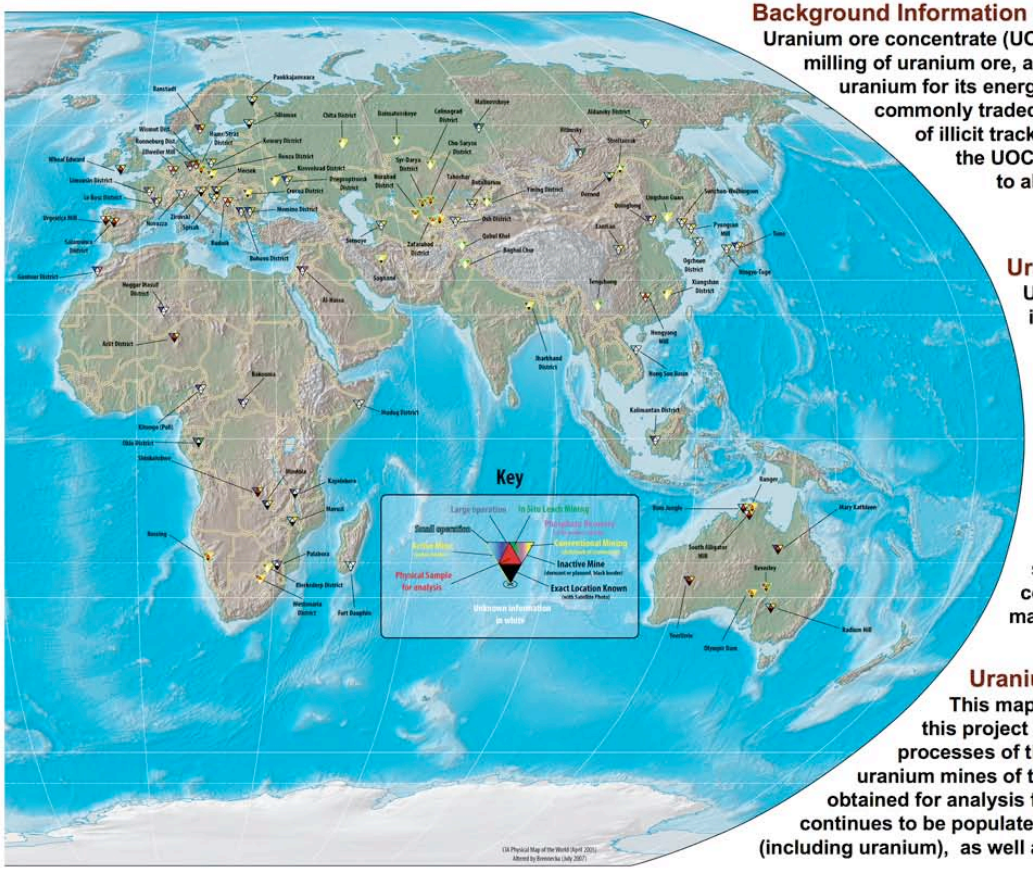
Summer Students 2008

Student	Major	University	Year
Greg Brennecka	Geochemistry	Arizona State Univ.	Grad
Alice Cheung	Nuclear Engineering	Georgia Tech	Grad
Kathryn Flynn	Geochemistry	UC Davis	Grad
Julie Gostic	Radiochemistry	U Nevada, Las Vegas	Grad
Martin Heller	Mathematics	Univ. South Carolina	Grad
Jordan Klingsporn	Chemistry	Univ. of Wisconsin	Undergrad
Kristina Lord	Mechanical Enginering	Iowa State Univ.	Grad
David Meier	Radiochemistry	Univ. of Missouri	Grad
David Sweeney	Nuclear Engineering	Texas A&M	Grad

Isotope Fingerprinting: Uranium Mines of the World

Gregory Brennecka – Nuclear Forensics Internship Program
Lars Borg – Chemistry, Materials, Earth and Life Sciences

Glenn T. Seaborg Institute



Background Information

Uranium ore concentrate (UOC), or "yellowcake", is the final product in the mining and milling of uranium ore, and represents an intermediate step in the utilization of uranium for its energy potential. Yellowcake is a fungible commodity that is commonly traded worldwide, but is also a regulated nuclear material. In cases of illicit tracking, chemical impurities and isotopic signatures imparted on the UOC by the source rock and/or mining process have the potential to allow the yellowcake to be traced to its point of origin.

Uranium Isotopes as a Forensics Tool

Uranium has three long-lived, naturally occurring isotopes, ^{238}U, ^{235}U and ^{234}U. Natural variability in these uranium isotopes compositions could make it possible to determine the specific depositional conditions of a uranium ore deposit and thus narrow down the possible source locations of illicit material.

Measurement Procedure

Measurements of the U isotopes are made on a Multi-Collector ICP-MS. In order to achieve the necessary precision on the measurements, the UOC sample is digested and the uranium chemically separated from the sample matrix. A $^{236}U/^{233}U$ double spike is added to each sample to correct for instrumental mass bias effects. These measurements will be made in the near future on samples collected for LLNL.

Drum of UOC or "yellowcake"

Uranium Mines of the World

This map (not fully shown) was created at LLNL for this project and contains the locations and mining processes of the active and historically productive (>1000 tU) uranium mines of the world. Physical UOC samples have been obtained for analysis from a number of these mines, and the database continues to be populated with data from multiple isotope systems (including uranium), as well as trace element concentration data.

Prepared by LLNL under Contract DE-AC52-07NA27344 Post #

Improved Reactor Simulations for Antineutrino Monitoring

Alice Cheung, Nuclear Forensics Internship

Glenn T. Seaborg Institute

A.Bernstein, N.S. Bowden, Advanced Detectors Group, LLNL

Georgia Institute of Technology

Abstract

Antineutrino detectors show great promise for reactor safeguards applications in directly measuring the thermal power as well as changes in fissile content of nuclear power reactors. The predicted antineutrino output from the reactor is vital to confirming the reactor operations and detector responses are valid. However, in the past, the simulations process has been tedious with many hours of manual file preparation required for each reactor fuel cycle simulation. To overcome this shortcoming, an automation process was developed that reduced the setup time required for each simulation. The automated process also allowed for more efficient extraction of results from the simulation output files. Automation with PERL scripts reduced the total preparation and data extraction time for the simulation by about a factor of five.

Antineutrino Safeguards and Monitoring

Cooperative Monitoring

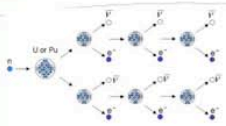
- The I.A.E.A. track the flow of fissile material through the civilian nuclear fuel cycle
- Current reactor safeguards involve
  - ✓Checking declarations
  - ✓Containment and surveillance
  - ✓Item accountancy
- Shortcomings
  - ✓Direct measurements of fissile content are normally not made
  - ✓when direct measurements are made, they are intrusive, expensive and only performed offline, before or after fuel is introduced in the reactor

Antineutrino Monitoring

- Determine operational status (On vs. Off)
  - 99% confidence within 5 hours
  - directly measure the thermal power of the reactor
    - 8.3% error for daily measurements
    - 3% error for weekly measurements
- Directly track or constrain fissile inventory of the reactor core in real time (weeks to months)
- Directly measure thermal power
- Detector is low maintenance, non-intrusive, and remotely deployable

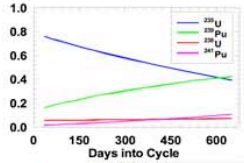
Antineutrinos in Reactors

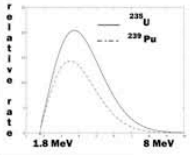
Antineutrinos from Fission



- About six antineutrinos are emitted per fission
- Detection rates near reactors are high:
  - e.g. 0.64 ton detector 25 meters from a 3.5 GWth reactor core will detect ~3800 events/day for a 100% efficient detector

Reactor Isotopics and Antineutrinos

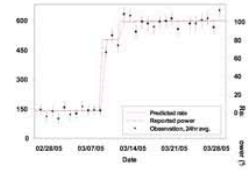




- Antineutrino rate and energy spectrum are sensitive to the isotopic composition of the reactor core
- Short term monitoring can measure reactor power
- Long term monitoring may be able to provide direct measurements of fissile inventory

Prototype Antineutrino Detector

- A prototype antineutrino detector has been deployed at SONGS (San Onofre Nuclear Generating Station)



- Reactor simulations are needed to predict and verify the data collected from the antineutrino detector

Reactor Simulations Using OrigenArp

OrigenArp

- Reactor simulations were performed on OrigenArp to determine the fission rates used to calculate the antineutrinos produced in the reactor
- OrigenArp is a Windows GUI written in C++ that facilitates the creation of ORIGEN-ARP and ORIGEN-S SCALE codes which solves the following equation:

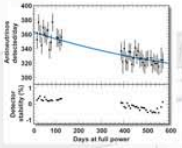
$$\frac{dN_i}{dt} = \sum_j \gamma_{ji}\sigma_{fj}N_j\phi + \sigma_{(i-1)\gamma}N_{(i-1)}\phi + \lambda_i'N_i' - \sigma_{fi}N_i\phi - \sigma_{i\gamma}N_i\phi - \lambda_i N_i$$

- ORIGEN-ARP: ARP stands for Automatic Rapid Processing and interpolates cross section libraries for ORIGEN-S
- ORIGEN-S: Designed to run depletion calculations

Sample OrigenArp Input

```
'This SCALE input file was generated by
'OrigenArp Version  5.1.01 March 22, 2007
=arp
w17x17
1.92172
1
392
25.681363
1
0.67
ft33f001
end
#origens
0$$ a4 33 e t
w17x17
3$$ 33 a3 1 0 a16 2 a33 0 e t
35$$ 0 t
54$$ 7 e
56$$ 6 6 a10 0 a13 5 a15 3 a18 1 e
57** 0 a3 1e-05 1 e t
Case 1
0.96372 MTU
58** 21.61 21.61 25.15 25.15 27.51 27.51
60** 65.5 131 196.5 262 327 392
66$$ a1 2 a5 2 a9 2 e
73$$ 922380 922350 942390 942400 942410
74** 945200 18520 5176 1348 944.5
75$$ 2 2 2 2 2
t
56$$ f0 t
end
```

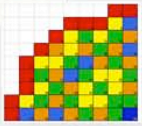
Simulation Shortcomings



- The observed rate from the detector deployed at SONGS matched the predicted rate from OrigenArp
- But the simulation process is tedious
  - Each assembly must be modeled one at a time
  - At least a quarter of the reactor core must be model if the core is symmetric
- To facilitate the input writing and execution of OrigenArp, a script was developed using PERL to automate the input writing and execution process and reduce the time to simulate a reactor

Optimization Results

- The automation PERL script requires the following files:
  - control.txt
  - power.txt
  - *.arp files for each fuel type present within the reactor
- The PERL script will read in the control.txt, read power.txt to write the input files for all the assemblies based on the fuel type and power density, execute all the files, and go through the output files to find the fission rates for U235, U238, Pu239, and Pu241 which are used later to find the antineutrino rates



- The 62 assemblies in a quarter of a LEU core would take roughly 2 hours and 35 minutes to simulate without automation
- The entire automation process (including making files for the automation process) would only take ~20 – 30 minutes

Conclusion

- Automation of writing and execution of input files has made reactor simulations ~5 times faster
- PERL script also sorts through the output files to extract the fission rates for nuclides of interest
- The script is easily modified to be used with other reactors as long as the cross section library exists in OrigenArp

Future Work

- PERL script should be tested for other reactor configurations
- Simulation should be benchmarked against reactor data
- Modify the PERL script to include further information beyond isotopics such as antineutrino density versus energy
- Automation process can be optimized further with more efficient coding
- Determine the cause for the discrepancy between the hand calculations of fission rates for the SONGS reactor core and the fission rates reported by OrigenArp

Acknowledgements: A.Misner and W.F.G van Roojien

Prepared by LLNL under Contract DE-AC52-07NA27344

Post #

Development of Automated Chemistry Methods for Heavy Element Research and Global Security Applications

Julie Gostic, Nuclear Forensics Internship Program
Roger Henderson[1], Dawn Shaughnessy[1], and Ken Moody[2]
[1]Chemical Sciences Division, CMELS and [2]AX Division, WCI

Glenn T. Seaborg Institute

UNLV UNIVERSITY OF NEVADA LAS VEGAS

INTRODUCTION AND MOTIVATION

Studying the nuclear and chemical properties of the transactinide or heavy elements provides validation of predicted periodic trends and illustrates the importance of relativistic effects as a causality for deviations in periodicity. Due to the relatively short lifetime of heavy element isotopes, and the low production probability, highly efficient automated chemistry becomes an integral component of successful chemical separation.

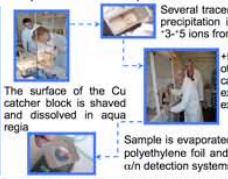
FORENSICS APPLICATIONS

Automation for the HE experiments can be translated directly to environmental forensics and monitoring work. The analytical system can be customized for trace amounts of material and easily modified for multi-sequential analysis purposes. A robust system with all the same commercial components is particularly desirable for field research.

Current (Labor Intensive) HE Method: From Production to Analysis

Step 1: Elemental and Isotopic Exploration

Step 3: Chemical Separation and Isolation



Several tracers are added and a co-precipitation is performed to isolate ^{3}-^{5} ions from the dissolved Cu

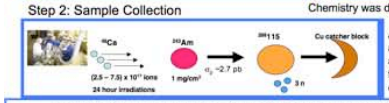
+5 ions are isolated from other constituents using cation exchange, anion exchange or reverse phase extraction chromatography.

The surface of the Cu catcher block is shaved and dissolved in aqua regia

Sample is evaporated onto a thin polyethylene foil and counted on α/n detection systems.

Chemistry was developed by PSI, FLNR and LLNL, performed at JINR

Step 2: Sample Collection



A thin foil ^{243}Am target is bombarded with ^{48}Ca ions at a dose rate of ~10^{18} ions/experiment. If the energetics and geometry of the compound nucleus are favorable, Element-115 is formed and the heavy element is captured onto a Cu catcher block.

HEAVY ELEMENT NUCLEAR AND CHEMICAL CHALLENGES

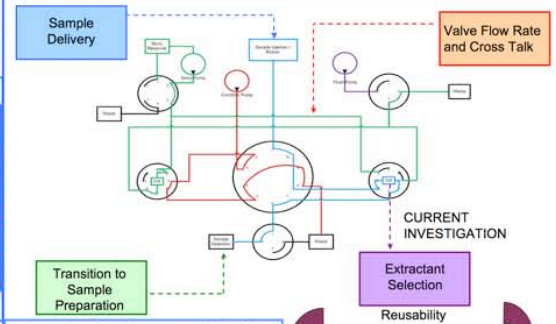
- Production rate is small, few atoms provided over production cycle.
- The nuclear life time ranges from 10^{-9} seconds to a few hours
- Chemistry system must be rapid, reliable, robust and highly efficient for ultra-trace type applications. (Automation is key!)

PROJECT GOALS

- Continue explorative research for the production of heavy elements.
- Develop a separation method that is suitable for heavy element chemistry and forensics applications.
- Incorporate the separation method into an automated flow-through injection system.

Chemistry • Materials • Earth • Life Sciences

METHOD AUTOMATION CHALLENGES



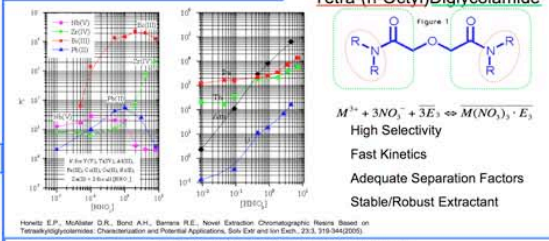
Developing Element 105 (Db) Chemistry

Isotopes of Ta, Nb, Pa have reasonable half-lives for developing +5 separation procedures

❑Which homolog will Db behave like in a given system?

DGA Extractant

Tetra-(n-Octyl)Diglycolamide



High Selectivity
Fast Kinetics
Adequate Separation Factors
Stable/Robust Extractant

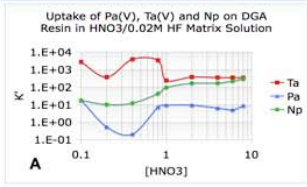
Horwitz E.P., McAlister D.R., Bond A.H., Barrans R.E., Novel Extraction Chromatographic Resins Based on Tetraalkyldiglycolamides: Characterization and Potential Applications, Solv Extr and Ion Exch., 23:3, 319-344(2005)

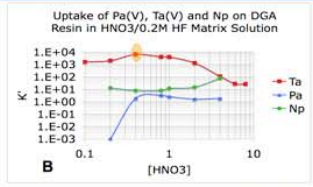
EXPERIMENTAL PROCEDURE

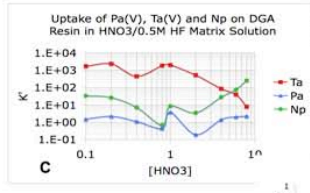
Determine the separation characteristics of +5 Homologs in HNO_3/HF solutions using DGA resin

- Batch Experiments: optimize matrix conditions [HNO3]/[HF]
  - 10 to 20 mg of resin per 1 mL of sample solution, 1 hour equilibration time
- Column Experiments: determine separation and isolation characteristics
  - 2 mL pre-packed DGA resin cartridges (Eichrom)
  - Mixed element systems (^{243}Am, ^{182}Ta, ^{233}Pa, ^{237}Np), sample volume 1 mL
  - Fraction (Eluent) volume 5 mL, flow rate 1-2 mL/min
- Activity verified by HPGe gamma spectroscopy

RESULTS







Figures A-C. The batch uptake (k') of the selected ions as a function of nitric acid media at constant [HF] on DGA resin (50-100 um) with a 1 hr equilibration time.

The batch experiment data shows that DGA selectivity is higher for Ta(V) vs Pa (V) and Np. The optimal loading condition for Ta/Pa is at 0.4 M HNO_3/ 0.2 M HF.

Sample Loading:
0.4 M HNO3/ 0.2 M HF, 1 m
Strip 1 (Pa):
0.4 M HNO3/0.02 M HF, 5 mL
Strip 2 (Ta):
8M HNO3/0.5 M HF
6 X 5 mL Fractions Collected
Strip 3 (Am):
0.1 M Ammonium Bioxalate, 5 mL

MS-2 Fractional Radionuclide Activity Distribution

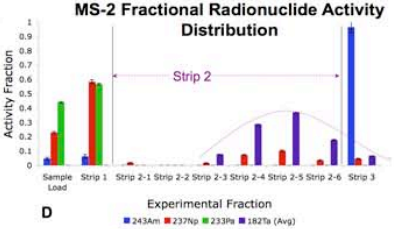


Figure D. Activity distribution of mixed radionuclides on 2 mL DGA resin cartridges,with a flow rate ~1 mL/min for all fractions.

FUTURE WORK

Using DGA resin for the separation and isolation of +5 Db homologs/pseudohomologs from other matrix constituents shows promise as a potential candidate for the automated heavy element chemistry platform. Additional studies will be conducted to further enhance this separation method and to test the fidelity of the resin after extended use.

The custom built in-line automation platform is currently in development at LLNL. It consists of off-the-shelf assembly components and is run by a LabView/PC platform. Mechanical and engineering issues, such as flow rate, column generation, valve cross talk, and resin compaction are being examined at this time.

This work was partially funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 08-ERD-030.

Prepared by LLNL under Contract DE-AC52-07NA27344 LLNL-POST-405946

Using Elemental Compositions to Predict the Origin of Yellow Cake

Martin Heller, Nuclear Forensics Internship Program

Martin Robel, CMELS and Chemical Sciences

Glenn T. Seaborg Institute

Abstract: Production of yellow cake is a multi-step process. (Figure 1 displays the refinement process.) Differences in raw ore from various mines as well as differences between refinement processes leads to different elemental compositions of the resulting yellow cake product. This research investigates whether various classification algorithms may be used to accurately predict the location of the mine which produced the original material.

Fig 1: Yellow cake production process

Introduction:

Figure 2: Yellow Cake

Yellow cake (Figure 2) is a refinement of uranium ore consisting of 70-90% U_3O_8. Yellow cake may be enriched to provide fuel for nuclear reactors, or material for nuclear weapons. Control of the material is essential for maintaining security.

Methodology:

Classification algorithms will be used to try to find a relationship between the distribution of elements in a sample of Yellow Cake and the mine where the sample originated from. The goal of a classification algorithm is to find a function which maps the data to a predicted class (see diagram 1) while minimizing some measure of error.

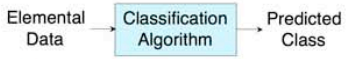


Diagram 1: General Classification Algorithm

•The predictions will only be useful if the sample is from one of the mines present in the training dataset. The false negative and false positive rates present in Table 2 give an assessment of reliability of the algorithms.

•This is not a good way to give evidence that a sample is not from a specific mine or country. If verification of a source is the goal, one should compare to a reference distribution for only the specific mine. This will reduce the false negative rate. If one finds that a sample is unlikely to be from the specified location, one may then use the appropriate algorithm to predict the origin.

The Data:

There are two separate data sets being analyzed in this investigation.

• **REF** consists of 1717 yellow cake samples from 22 different mines from 8 different countries measured by an outside source. Each sample has had 30 elements measured in ppm. This sample will be used to fit the various classification algorithms.

• **LLNL** consists of 20 samples from 20 different mines corresponding to mines present in the REF dataset. Sixteen of the elements correspond to those in the REF dataset. These will be used to test the classification algorithms.

A test for a difference in measurements is presented in Table 1.

Table 1: The datasets in REF and LLNL were gathered by two separate labs. A check was performed to see if the data is similar for each of the labs. The results for these tests are presented to the left.

Element	Mean Difference	Two-sided p-Val
Ag	0.12	0.28
Ba	-2.82	0.11
Ca	-432.30	0.24
Cd	-3.03	0.16
Cr	-0.67	0.64
Fe	484.68	0.39
K	-302.65	0.31
Mg	-65.03	0.10
Mo	-94.13	0.01
Na	228.65	0.69
Pb	-0.72	0.30
Th	-62.31	0.28
Ti	-4.19	0.04
V	-18.20	0.04
Zr	141.65	0.31

New Classification Algorithm:

A new classification algorithm was devised termed Iterative Partial Least Squares-Discriminant Analysis (IPLSDA). When attempting to predict the the class of an unknown sample it fits a Partial Least Squares-Discriminant Analysis (PLSDA) model to the data in each iteration. At each iteration, classes which are unlikely are removed from the training set, then the PLSDA model is refit. The iterations continue until the class of the unknown unknown is clear. To test its effectiveness, it will be tested against Classification Trees (CT). The CT algorithm converges asymptotically to the likelihood ratio for nearly any classification problem. The likelihood ratio is nice since it is a uniformly most powerful test. On the other hand, IPLSDA converges to a modified linear discriminant analysis classification rule which is not uniformly most powerful.

Fig 3: Classification Tree

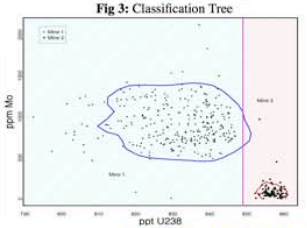
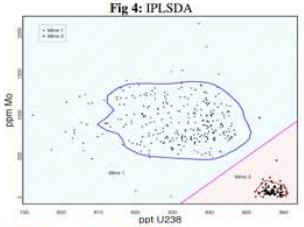


Fig 4: IPLSDA



Results and Confusion Matrices for REF:

To summarize the results of the analysis of the REF dataset, confusion matrices were used. Confusion matrices are a nice visual way to see how errors are presented.

CT Predicted (Actual Countries)

Country	1	2	3	4	5	6	7	8	Total	False Positive
1	104	4	1	1	0	0	0	0	110	0.05
2	3	399	2	0	2	1	2	0	409	0.02
3	8	2	673	1	2	12	10	0	708	0.05
4	0	1	2	58	0	0	0	0	61	0.05
5	0	0	0	3	173	0	0	0	176	0.02
6	3	0	1	0	0	42	0	0	46	0.09
7	5	4	10	2	0	1	147	0	169	0.13
8	0	1	0	0	0	0	10	27	38	0.29
Total	123	411	689	65	177	56	169	27	1717	
False Negative	0.15	0.03	0.02	0.11	0.02	0.25	0.13	0.00		

IPLSDA Predicted (Actual Country)

Country	1	2	3	4	5	6	7	8	Total	False Positive
N/A	0	0	1	0	0	0	1	0	2	1.00
1	117	3	2	0	0	4	0	5	131	0.11
2	1	392	1	0	8	1	5	0	408	0.04
3	2	2	610	2	0	2	2	0	620	0.02
4	0	0	29	54	6	0	2	0	91	0.41
5	0	0	0	7	161	0	0	0	168	0.04
6	3	2	31	0	0	49	1	0	86	0.43
7	0	12	15	2	2	0	158	0	189	0.16
8	0	0	0	0	0	0	0	22	22	0.00
Total	123	411	689	65	177	56	169	27	1717	
False Negative	0.05	0.05	0.11	0.17	0.09	0.13	0.07	0.19		

Table 2: Confusion matrices for the analysis of the REF data set using the CT and IPLSDA algorithms. The values along the diagonals correspond to correct predictions. The values in the other cells show how errors are made. These errors are summarized in the margins. False negatives correspond to misclassifying a sample from country A as another country. False positives correspond to the probability that a sample predicted to be from a certain country is actually from another country.

Least Important	Most Important
U-235	Si/SiO2
Ag*	U-234*
F-	Na*
Cd*	As
Pb*	Th*
Z	Ti*
Cr*	Fe*

Table 3: The most and least important elements for the IPLSDA analysis of REF are listed to the right. The *'s are used to indicate the presence of the measurements in the LLNL data set. Including the unstarred elements in the 'Most Important' column could lead to an increased accuracy.

Test of the LLNL Dataset:

The prediction accuracies (1-false positive) realized for analysis of LLNL in Table 4 are far lower than those expected from the analysis of REF. Linear corrections equivalent to the mean shifts presented in Table 1 were attempted with little increase in accuracy. In contrast to the results of the analysis of REF, there is a significant preference for the IPLSDA algorithm.

	IPLSDA	CT
Country	0.8	0.75
Mine	0.6	0.45

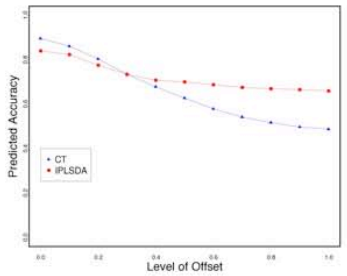
Table 4: Accuracies realized for the LLNL dataset.

The disparity in results are partially due to the differences in distribution of mines in the REF and LLNL data set. As the false negative rate is independent of the distribution of the mines, they are similar to the observed results.

Robustness Analysis:

The analysis of the LLNL data suggests that the IPLSDA algorithm is more robust to deviance in population distribution than the CT algorithm is. Altering the parameters used for fitting the CT algorithm cause the algorithms to perform more similarly, but this is cheating since it uses information from the LLNL dataset. A simulation showing the results of shifting the mean value on the overall prediction accuracy are displayed in Figure 5.

Figure 5: Displays the effects on the prediction accuracy by offsetting the data in the samples used for prediction. This was performed by using the 16 elements present in both LLNL and REF. Each data point represents a cross validation where each prediction is based on the true value plus an offset. The offset has the mean (Level of Offset)*(value in Table 1).



Current / Future Work:

• Currently working on a paper quantifying the robustness of the IPLSDA algorithm from a theoretical perspective in relatively small samples using multivariate gamma distributions.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Pu and U Partitioning on Colloids in Nevada Test Site Groundwater: Implications for Radionuclide Transport

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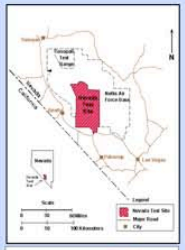
Nuclear Forensics Internship Program, Glenn T. Seaborg Institute, CMELS
Pihong Zhao, Ross Williams, Mavrik Zavarin, Sarah Roberts, and Annie Kersting
Lawrence Livermore National Laboratory

Glenn T. Seaborg Institute

UCDAVIS GEOAGGIES

Introduction



Underground nuclear explosions at the Nevada Test Site (NTS) are a source of radionuclide contamination in the environment that can potentially be mobilized by groundwater. Low solubility radionuclides including Pu and other actinides can be transported in aquifers by mineral colloids (< 1000 nm sized particles).

The objective of this study is to determine how plutonium and uranium are distributed between the solid (colloid) and dissolved phases of groundwater, and to compare how the size, composition, and surface area of the colloids affect Pu and U sorption.

Groundwater for this study was collected from the Chancellor test site at Pahute Mesa, NTS.

Methods

Multiple techniques were used to analyze Pu and U in the colloids and characterize their mineralogy and surface area:

- Colloids were settled, centrifuged, and filtered out of the water sample and weighed(see sample preparation).
- Pu and U were extracted from each size fraction by ion exchange chemistry.
- The Isoprobe Inductively Coupled Mass Spectrometer analyzed Pu and U concentrations after the chemical extraction.
- Mineral composition was determined by X-ray diffraction.
- Colloids of each size fraction were prepared for surface area analysis by the B.E.T. method.

Sample Preparation

Colloid Fraction: >1000 nm | 100-1000 nm | 10-100 nm

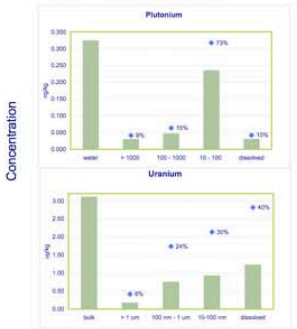
Method:
- Particle settling from well sample (55 hours).
- Centrifuging supernatant 1 (56 hours).
- Filtering supernatant 2 (72 hours).

Radionuclide Partitioning

Pu is dominantly associated with the 100 - 1000 nm colloid fraction, which has 73% of the total Pu. The other size fractions of solids have sorbed Pu at lower levels. Only 10% of the Pu was partitioned into the dissolved phase.

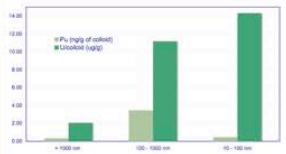
U is distributed equally on the < 1000 nm colloids, though 40% of the total U is in the dissolved phase.

Nuclide Distribution



Size Fraction (nm)
Diamonds are percent of total.

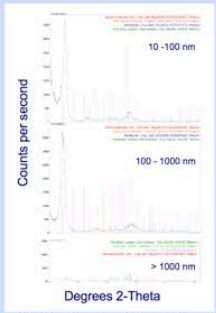
Nuclide Affinity



Size Fraction (nm)

The 100 - 1000 nm size fraction has 3.46 ng of Pu per gram of colloid, compared to < 5 ng for the other fractions. The U concentration has a direct relationship with the solid size fraction.

Characterizing Colloid Mineralogy



XRD spectra of each size fraction.

The colloid composition in the groundwater consists of clays, zeolites, and detrital feldspar. The clay and zeolites are common secondary minerals in NTS groundwater, and probably carry most of the radionuclides.

The large solid fraction contains fewer secondary minerals which correlates with its lower Pu and U. The 2 other fractions may have distinct clay compositions (illite vs. montmorillonite) but further work is needed to quantify the differences and relate them to radionuclide affinity.

Conclusions

-Pu in groundwater is strongly partitioned onto the colloid fraction and not in the dissolved phase.

- In this aquifer, the size of the colloids controls Pu and U sorption, and the mineralogy of colloids may have an impact.

-These results confirm previous work that shows the transport of Pu occurs on colloids and not in the dissolved state.

-Contrary to previous assumptions, the U in the system is sorbed onto colloids as well as being present in the dissolved phase.

- The Pu and U data show that transport models need to incorporate colloids in order to model radionuclide transport correctly.

Future Work

The next step is to analyze the impact of particle surface area on partitioning, and study how partitioning evolves in groundwater flow down gradient.

Chemistry • Materials • Earth • Life Sciences

Prepared by LLNL under Contract DE-AC52-07NA27344

LLNL-Post-406213

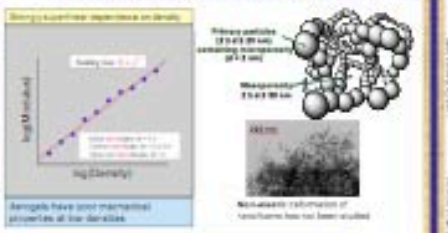
Nanomechanics of Ultra-Low Density Nanoporous Solids

Kristina A. Lord, Nuclear Forensics Internship Program

Sergei O. Kucheyev, MSTD, CMELS

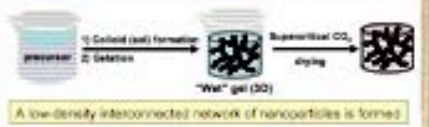
Glenn T. Seaborg Institute

Poor mechanical properties limit applications of low-density foams



Lacking fundamental understanding of mechanical deformation of low-density nanofoams

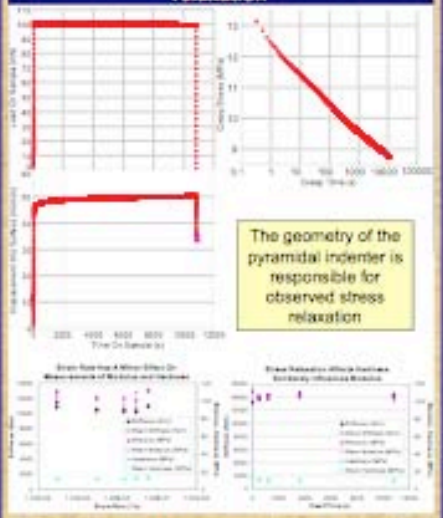
Synthesis of low-density foams



A low-density interconnected network of nanoparticles is formed

We use low-load, large-displacement indentation to study nanomechanics of foams

Silica nanofoams exhibit stress relaxation



The geometry of the pyramidal indenter is responsible for observed stress relaxation

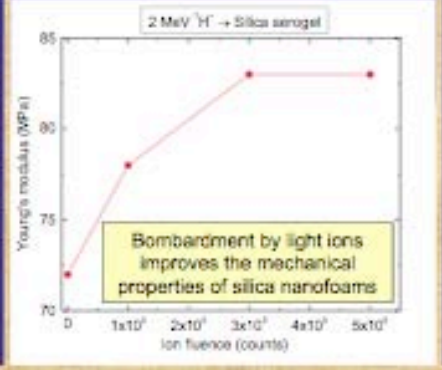
Silica nanofoams exhibit logarithmic stress relaxation

Stress Relaxation rate is independent of maximum load

We observe room temperature creep of nanoporous glass

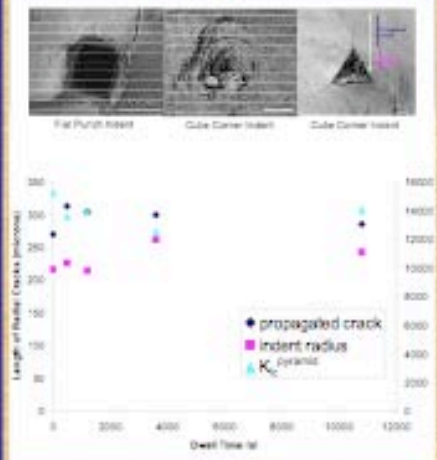
Creep rate is dependent on maximum load

Ion bombardment could be used to improve mechanical properties of nanoporous solids



Bombardment by light ions improves the mechanical properties of silica nanofoams

Fracture toughness measurements are not affected by creep



Summary

1) Results of nanoindentation of ultra-low density silica nanofoams are very sensitive to indenter geometry (stress and strain fields).
2) Stress relaxation and creep phenomena are observed in room temperature indentation of ultra-low density silica nanofoams.
3) Mechanical properties of silica nanofoams can be modified by ion bombardment.

Chemistry · Materials · Earth · Life Sciences

Prepared by LLNL under Contract DE-AC52-07NA27344

Post #

Secondary Ion Mass Spectrometer Resurrection

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Doug Phinney, Chemical Sciences Division of CMELS

Glenn T. Seaborg Institute

University of Wisconsin Green Bay

ABSTRACT

This internship used an ion probe to perform isotopic-ratio analysis using secondary ion mass spectrometry techniques. A second project consisted of achieving a vacuum in a nonworking ion probe, which was a major step in the return of this ion probe back to service. The isotopic-ratio measurements were performed for lithium isotopes in two aluminum samples. One aluminum sample came from a nuclear reactor, and the other was a piece of unirradiated aluminum. These samples showed the effect of neutron fluence on the isotopic ratio due to the neutron capture on lithium and boron. Work will continue so that the non-functional ion probe can obtain vacuum down to ultra-high vacuum levels.

INTRODUCTION

Ion microprobes are sputtering-source mass spectrometers. Such mass spectrometers are called secondary ion mass spectrometry (SIMS) instruments, because the sputtered ions are separated and counted mass spectrometrically. Ion probes are used to study microscopic structures for trace-element concentrations and isotopic ratios. These capabilities are particularly useful for nuclear-forensic applications.

This internship focused on two ion probe projects:

1. Resurrecting a non-working ion probe named Panurge (figure six)
2. Acquiring isotopic-ratio data on a working ion probe called the LLNL 3f (figure four)

The main objective of the Panurge project was to recondition the vacuum system and obtain ultra-high vacuum. This is an important initial step in returning Panurge to a state where it can be used for isotopic and trace-element analysis.

Figure 1: Panurge after vacuum connections were in place.

Figure 2: Primary column of Panurge

Figure 3: Forepumps for Panurge

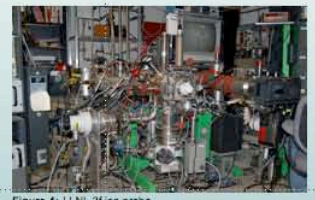

Figure 4: LLNL 3f ion probe

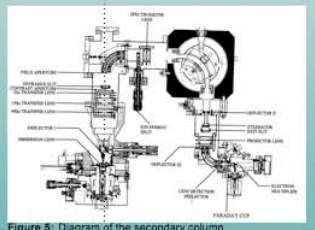

Figure 5: Diagram of the secondary column (mass separating) section of Panurge

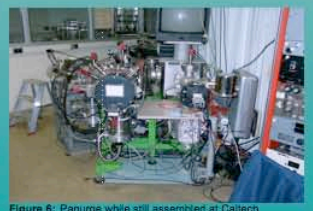

Figure 6: Panurge while still assembled at Caltech

RESURRECTING PANURGE

Obtaining ultra-high vacuum required several Panurge electronic systems to be reconditioned and made operational. The first task was to document all custom modifications to Panurge and to repair the chassis that controls Panurge's vacuum operation. This chassis had multiple modifications and several safety deficiencies that needed to be fixed before operation. Once the safety concerns were fixed, the chassis was re-inspected and approved for use.

Panurge has three forepumps (figure three). In this project, all three forepumps were connected to their respective forelines, and Convectron gauges were added to monitor the foreline pressures. Once the forepumping system was finished, one of the forepumps was operated to test the vacuum integrity of its foreline.

The next step involved connecting the forelines to the Panurge. The venting system was also installed at this time. Cleaning and installing many components such as turbo-molecular pumps, apertures, and several sections of the primary column was necessary to close the system so vacuum could be achieved.

On July 22, 2008 vacuum down to twenty millitorr was achieved in Panurge indicating no major leaks were present.

DATA AND ANALYSIS

The LLNL 3f ion probe was used to analyze two samples of aluminum to determine the isotopic ratio of ^{7}Li to ^{6}Li. The first sample was unirradiated aluminum and showed a normal lithium ratio of 12.28:1 (figure eight). The second sample was obtained from a nuclear reactor and was found to have a ratio of 38.13:1 (figure nine). In the reactor sample, lithium associated with boron inclusions showed a very high ratio of 281.67:1. The sample from the nuclear reactor shows skewed ratios of ^{7}Li to ^{6}Li because of high neutron fluence. Two processes dominate the change in the ratio.

$$^{6}Li + n \rightarrow {}^{3}H + \alpha \text{ (decreases } {}^{6}Li)$$
$$^{10}B + n \rightarrow {}^{7}Li + \alpha \text{ (increases } {}^{7}Li)$$

Isotopic-ratio data from essentially the whole Periodic Table can be collected using an ion probe. Such data are useful for nuclear-forensics applications because they can be used as an indicator of the total neutron flux in a nuclear reactor.

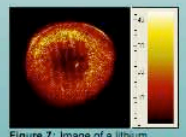

Figure 7: Image of a lithium inclusion using a resistive anode encoder on the LLNL 3f ion probe

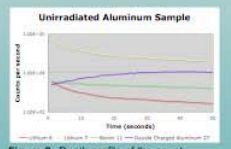

Figure 8: Depth profile of the count rate of four mass species for the unirradiated aluminum sample

Figure 9: Depth profile of the count rates of four mass species in the reactor aluminum sample

FUTURE WORK

Currently the cooling system for Panurge is being installed along with flow gauges. Once this is completed, the venting system will be connected to the facility argon-gas system.

Although vacuum has been achieved, ultra-high vacuum has not been achieved as of this point. Ultra-high vacuum requires turbo-molecular pumps; the controllers for these pumps need to be inspected for electrical safety compliance. Once ultra-high vacuum is obtained, the only remaining work to be performed on the vacuum system is to activate the ion pumps and ensure all of the systems have adequate vacuum gauging.

Achieving ultra-high vacuum is just the first step in returning the ion probe to operation. Completely resurrecting Panurge requires that the ion optics and the magnet-controlling systems are operational.

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344

Post #

Cosmogenic ^{35}S as a Tracer of Hydrologic Processes in Alpine Basins

David Meier (Nuclear Forensics Intern Program, U. Missouri)

Bradley K. Esser, Richard Bibby, Everett Guthrie, Mike Singleton, & Jean Moran (CSD/CMELS)

Glenn T. Seaborg Institute

Prepared by LLNL under
Contract DE-AC52-07NA27344

Project Goals

I. Implement standard methods at LLNL for low-level determination of ^{35}S in environmental waters

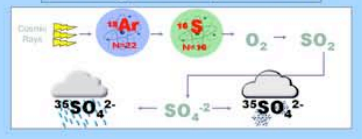
II. Participate in field sampling & analysis of alpine streams and groundwaters for S-35

III. Develop a new method for ^{35}S analysis of high-sulfate surface and ground water.

Sulfur-35 as an environmental tracer

- Sulfur-35 is a soft beta emitter with a half-life (87 days) suitable for studying processes on weeks to 1-2 year time scales. Such processes include
  - Snowmelt, stream runoff and acid anion cycling in alpine basins
  - Rapid recharge in managed aquifer systems
- Sulfur-35 is produced cosmogenically in the upper atmosphere. Production rates are low, and large volume water samples are necessary for analysis

Cosmogenic ^{35}S production



I. Implementation of Standard Method for Determination of Sulfate-^{35}S

Method

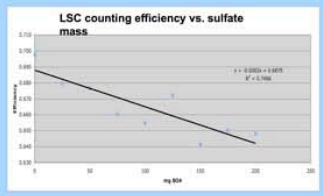
- **Collect large volume water sample**: In field, filter up to 20 L of water into a polyethylene carboy
- **Use ion exchange to extract sulfate from water:** Back at lab, pass sample through an anion exchange resin (Amberlite 400 in Cl form). This step reduces volume by a factor of 50: from ~20L to 100mL.
- **Precipitate sulfate as barium sulfate:** Mix eluant with barium chloride and precipitate barium sulfate
- **Suspend barium sulfate in liquid scintillation cocktail:** Up to 200 mg of sulfate (~500 mg barium sulfate) can be suspended)
- **Count using low-level LSC to determine ^{35}S activity:** Quantulus 1220 LSC or Packard Tri-Carb 3100TR

Initial Results

- Chemical yield for ion exchange & barium sulfate precipitation
- Analysis parameters: Packard Tri-Carb 3100TR; window 4-80 keV, 120 minutes,
- Counting efficiency: 50-62% for up to 200 mg sulfate
- LLD: 1.4 mBq, 0.1 mBq/L for 20-L sample, 0.3 mBq/mg SO_4^{2-}

Comparison with Previous Research

- Our current detection limit compares wells with reported literature values (see below)
  - DL as mBq ^{35}S/L water: 0.5 mBq/L (Burns et al, 1998)
- Sulfur-35 activities measured in rainfall and in alpine stream samples (see next panel), also compares well to previous studies reported in the literature (see below), especially in comparison to Rocky Mountain sites (average stream: 1.3 mBq/L this study; 1.2 mB/L Loch Vale, CO)
  - Rainfall & Snow: 5-50 mBq/L (Hong et al, 2005; Suecker et al, 1999; Michel et al, 2000);
  - Alpine Streams & Springs: non-detect to 50 mBq/L (Shanley et al, 2005; Suecker et al, 1999; Michel et al, 2000);



II. ^{35}S as a tracer of alpine hydrologic processes

Sulfur-35 (half-life=87 days) as a groundwater tracer

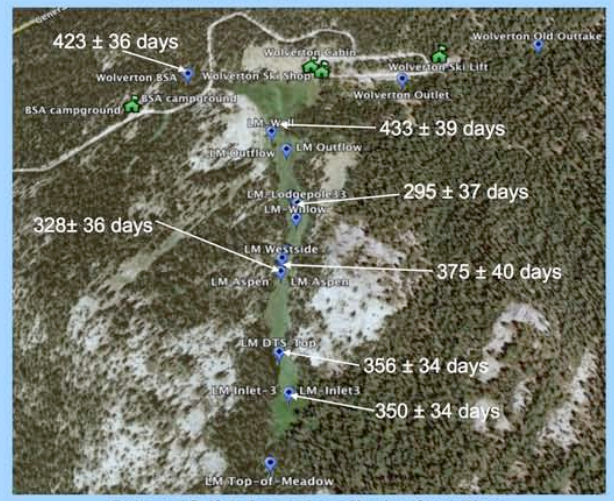
The goal of this research is to fill a critical gap in the understanding of groundwater dynamics in Sierra Nevada alpine basins. These systems may be important in controlling hydrologic response of California headwater basins to climate change, which is predicted to result in more rain and earlier snow-melt. Current methods involving tritium dating (half-life = 12.1 years) cannot resolve young age components from recent recharge (<2 years). Sulfur-35 is being utilized to constrain water and solute residence times and sources in alpine basin hydrologic systems (surface water, groundwater & snowpack)

Long Meadow, Wolverton, Sequoia National Park

- Critical Zone site (significant transition from snow to rain with climate change)
- Intensively studied and instrumented by Roger Bales and Martha Conklin (UC-Merced)
- Samples collected in early July in collaboration with several other groups, including Scott Tyler (UNR)

Site	Collection Date	$[SO_4^{2-}]$ mg/L	Liters processed	Sulfate spike added	$[^{35}SO_4^{2-}]$ mBq/L	$[^{35}SO_4^{2-}]/[SO_4^{2-}]$ mBq/mg
Wolverton Well	7/8/08	0.51	15.7	100 mg	1.29	2.52
Inlet 3	7/8/08	0.3	18	100 mg	1.47	4.88
DTS top	7/8/08	0.31	18.5	100 mg	1.45	4.69
Aspen	7/8/08	0.23	18.1	100 mg	1.35	5.85
Met Pine	7/9/08	0.17	18	100 mg	1.29	7.57
Shooting Star	7/9/09	0.27	18	100 mg	1.08	4.00
Wolverton outlet	7/10/08	0.45	19.5	100 mg	1.23	2.74
Rain Water	7/10/08	6.4	17.5	0 mg	24.46	81.52

Note: Measured rainwater sulfate includes dry deposition; calculated rainwater ^{35}S/sulfate uses average sulfate for Sequoia NP precipitation (Clow et al, 2003).



Estimated Sulfate Ages in Long Meadow Creek Waters

- Initial assumed to be rainwater from July 10, 2008 event
- Stream water activity normalized to measured sulfate concentration; rainwater activity normalized to average sulfate concentration for Sequoia NP precipitation (Clow et al, 2003)
- Estimated ages agree with range of ages found in Colorado alpine basins (e.g. Suecker et al, 1999)

III. Development of a New ^{35}S Method

Managed Aquifer Recharge

Sulfur-35 is potentially an useful tracer of rapid recharge in managed aquifer systems for three reasons:

- ^{35}S has a half-life appropriate for recharge time scales (weeks to 1 yr)
- ^{35}S occurs naturally, and continuously introduced into the system
- In oxic systems on fast timescales, sulfate reactions are well understood

The challenge is detecting ^{35}S is high-sulfate groundwaters where most of the sulfate (from weathering or pollution) is old and dead.

Limitations of the Current Method

- The current method is adequate for processing **up to 200 mg of sulfate** for determination of ^{35}S. Counting efficiency falls rapidly above 200 mg.
- Typical sulfate concentrations in environmental waters
  - Alpine streams and rainfall: 0.2 to 5 mg/L
  - Lowland streams and rivers: 10-100 mg/L
  - Polluted rivers and groundwater: 100-300 mg/L
- For low-sulfate water, detection of ^{35}S is limited by the amount of water that can be collected and processed, e.g. **20 L of alpine stream water** with 0.5 ppm sulfate yields 10 mg of sulfate
- For high-sulfate waters, detection of ^{35}S is limited by the amount of sulfur that can counted, e.g. **1 L of groundwater** with 200 mg/L sulfate yields 200 mg sulfate, the maximum load for the current method

Proposed Method for High-Sulfate Waters

Proposed method circumvents counting inefficiencies by reducing the sulfur in $BaSO_4$ to H_2S (g) which is collected and counted as HS^- ions. With this approach, we can analyze much larger volumes of high-sulfate river and groundwater.

- In a 250 mL dual necked flask, 2g $BaSO_4$, 15 g $SN_2P_2O_7$ and 150 mL of 85% H_3PO_4 are combined.
- A 1M NaOH solution is placed in the primary scrubber and via an inlet in the flask, introduce argon gas at a rate of 100 ml/min.
- Using a heating mantle, heat the flask until the sample becomes transparent and viscous.

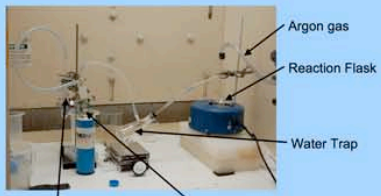
$$BaSO_4 + Sn_2P_2O_7 + H_3PO_4 \xrightarrow{-H_2O} H_2S + SnO_2 + P_2O_5$$

Preliminary Results

For a 10 g barium sulfate sample, we were able to

- Convert 75% of the barium sulfate to sulfide form
- Achieve a counting efficiency of 90%

This allows us to count **15 times** as much sulfur per sample



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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344

Post #

Development of Isotopic Taggants for Uranium Fuel

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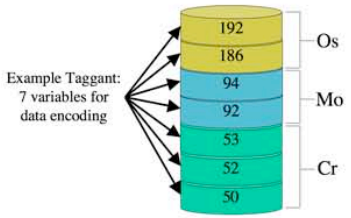
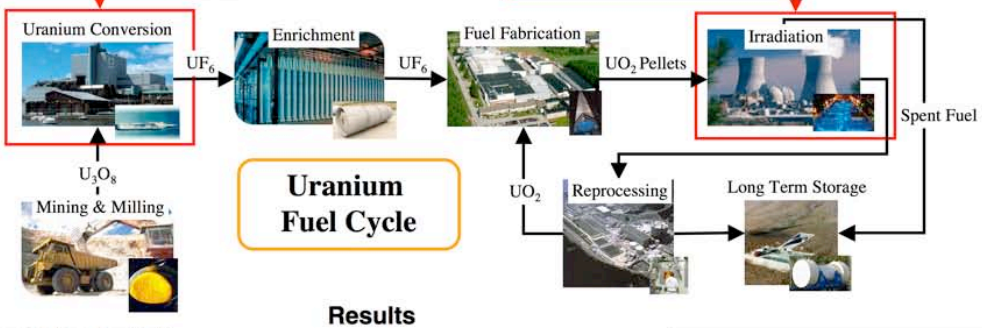
NSSPI NUCLEAR SECURITY SCIENCE & POLICY INSTITUTE

***Abstract:** As part of the effort to improve proliferation safeguards and nuclear forensics for the 21st century, we are seeking to develop an identification tag or taggant for uranium fuel that cannot be removed or forged. Various elemental impurities embedded within the fuel in known concentrations and with varying isotopic composition could serve as the desired taggants. The isotopic composition of such taggants could reveal the origin of diverted fuel while unexpected changes in the concentration of the taggant in known fuel could reveal whether undeclared material had been processed through fuel cycle facilities. Research was done to evaluate the behavior of potential isotopic taggants through certain fuel cycle processes.*

Introduction

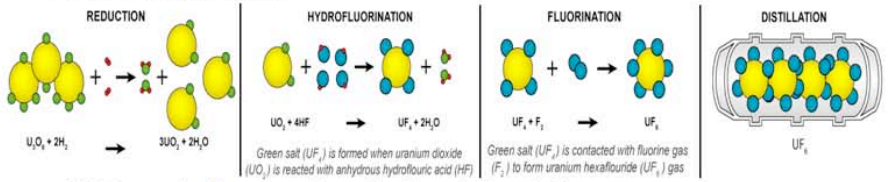
- Desire an ID tag or taggant for uranium fuel that:
  - Is difficult to remove
    - Taggants to be disbursed in fuel
  - Is difficult to forge
    - Data encoded in taggant by varying isotopic concentrations of elemental impurities
  - Can remain with Uranium through all fuel cycle processes
    - Taggants evaluated for survivability through irradiation and ore conversion





Methods

- Irradiation Analysis
  - Irradiation degradation assumed to be primary taggant limitation
  - Simulations done with ORIGEN-ARP
    - Impurities added to fuel in 100 ppm concentrations
    - Fuel irradiated to 35 GWD/MTU
- Conversion Chemistry Analysis
  - Taggants must have similar chemistry to Uranium to persist during conversion
  - Dry Conversion Process:



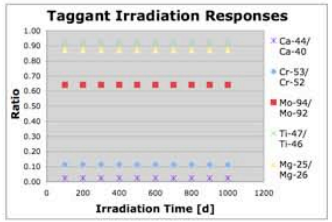
  - Wet Conversion Process: adds purification prior to reduction

Digestion	Precipitation	Calcination
$U_3O_8+8HNO_3 \rightarrow 3UO_2(NO_3)2+2NO_2+4H_2O$	$2UO_2(NO_3)_2+6NH_4OH \rightarrow (NH_4)_2U_2O_7+4NH_4O_3+3H_2O$ $(NH_4)_2U_2O_7+Heat \rightarrow UO_3$	$6UO_3*1/2H_2O \rightarrow 2U_3O_8+O_2+3H_2O$

Results

- Irradiation Analysis
  - Elements (# of isotopes) with concentrations varying less than 2% during irradiation:
    - C(2), N(1), Ne(3), Mg(3), Si(3), S(3), Cl(1), Ar(3), K(2), Ca(6), Ti(4), V(1), Cr(1), Fe(2), Ni(3), Cu(2), Zn(5), Ga(1), Ge(3), Kr(1), Sr(1), Mo(2), Ru(2), Pd(1), Cd(2), Sn(1), Sb(1), Te(2), Ba(1), Ce(1), Sm(1), Yb(1), Os(2), Pt(1), Hg(1), Tl(1), Pb(2)
- Conversion Analysis: ex. Molybdenum & Chromium

Element	Oxidation States	Compounds Formed						
U	III, IV, V, VI	$UO_2(NO_3)_2$	$(NH_4)_2U_2O_7$	UO_3	U_3O_8	UO_2	UF_4	UF_6
Mo	III, IV, V, VI	XX	$(NH_4)_2Mo_2O_7$	MoO_3	XX	MoO_2	MoF_4	MoF_6
Cr	II, III, IV, VI	$Cr(NO_3)_3$	$(NH_4)_2Cr_2O_7$	CrO_3	XX	CrO_2	CrF_4	XX



Discussion

- Isotopic taggants could reveal origin of diverted material
- Variation in or absence of taggant in Uranium stream(s) at a fuel cycle facility could denote processing of undeclared material
- Ample potential taggants exist that do not appreciably vary during irradiation
- Multiple taggants added at different process stages may be necessary to fully trace Uranium through Uranium Conversion and other chemical processes

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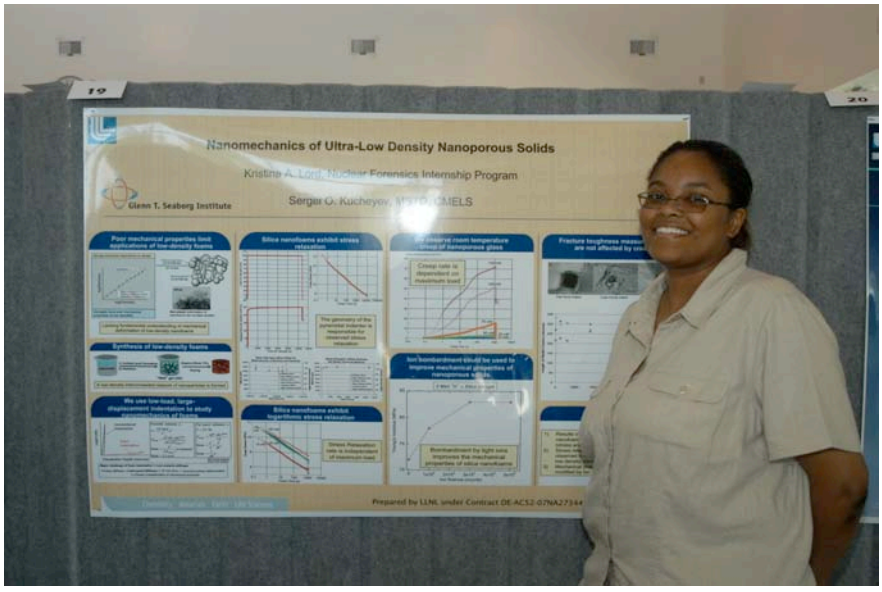
Prepared by LLNL under Contract DE-AC52-07NA27344

LLNL-POST-406103

Summer students at work, 2008

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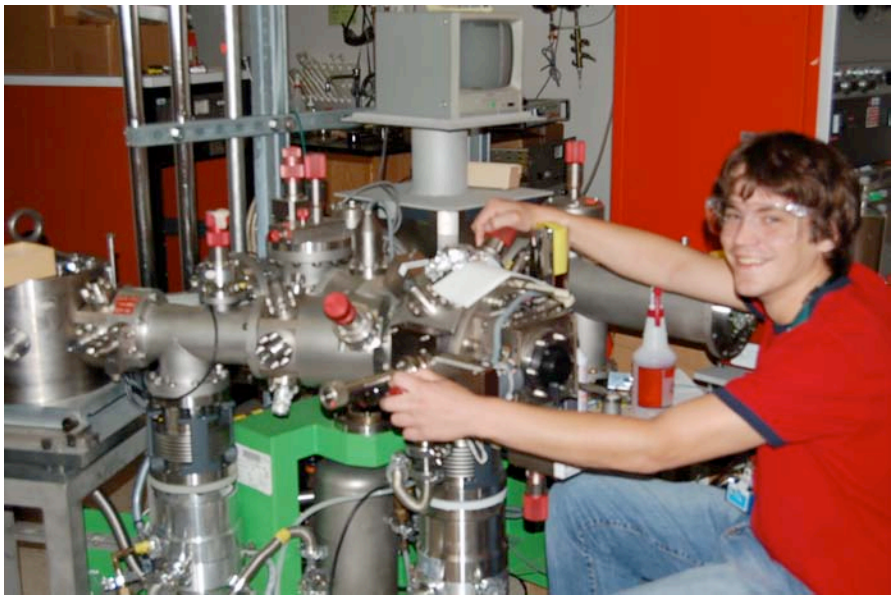

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